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Inhibition of steel corrosion with imidazolium-based compounds

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Motivation - to model the experiment

The aim of this work is to supplement the investigation of the corrosion inhibition by the family of organic compounds (viz. 1-actyl-3-methylimidazolium with addtional hydrogensulphate, chloride, and bromide) by quantum-chemical calculations, and thus to prepare a framework to predict inhibitor-like properties in designed compounds. To achieve this objective we prepare a realistic model of a single molecule on iron surface Fe(110) by employing the Vienna ab-initio Software Package [1], supplemented with the meta-GGA strongly-constrained and appropriately normed semilocal density functional to model the electronic structure properties of both free and bounded-to-surface molecules of 1-butyl-, 1-hexyl-, and 1-octyl-3-methylimizadolium bromide, chloride, and hydrogensulphate. From our calculations we extract the HOMO/LUMO gap, hardness, electronegativity, and charge transfer of electrons from/to molecules-in-question. It supports the experimental findings and explains the influence of the alkyl chain length and the functional group on the inhibition process.

Charge transfer and other properties

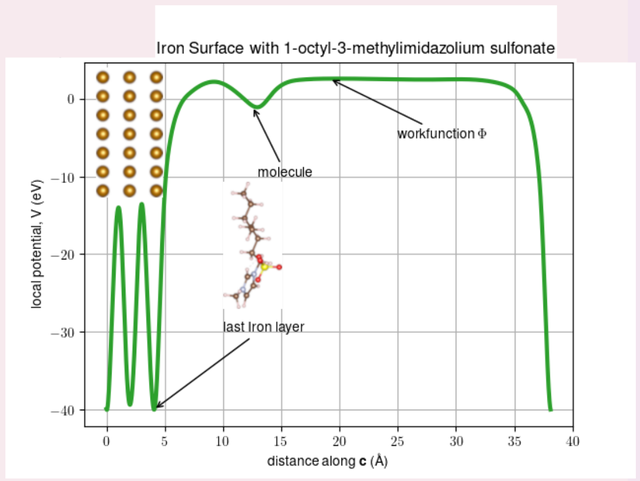
We assess the hardness (η) and electronegativity (χ) via the energies of the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO)

$$\eta \equiv \frac{1}{2}\left(-E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}\right),$$

$$\chi \equiv -\frac{1}{2}\left(E_{\mathrm{HOMO}} + E_{\mathrm{LUMO}}\right).$$

These quantities, coupled with the Fermi energy (E_F) and the so-called Workfunction (Φ) give first estimation of the charge transfer

$$\Delta N = N^e_{\mathrm{surface}} - N^e_{\mathrm{free}} \approx \frac{\chi_{\mathrm{Fe}} - \chi_{\mathrm{mol}}}{2(\eta_{\mathrm{Fe}} + \eta_{\mathrm{mol}})} \approx \frac{-(E_F - \Phi) - \chi_{\mathrm{mol}}}{2\eta_{\mathrm{mol}}}.$$

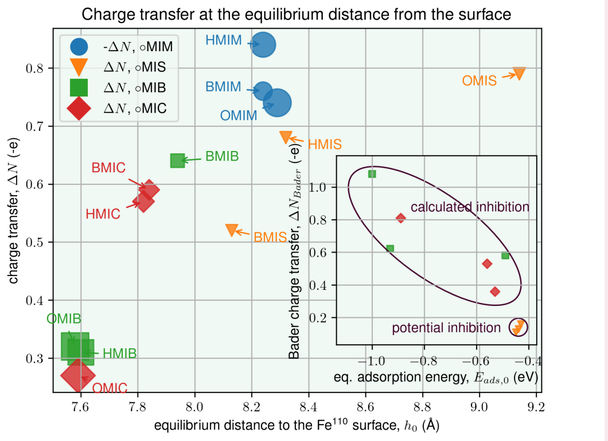


The local potential averaged along the 'vacuum' axis. Note the minima indicating the layers of Iron and the molecule, as well as the value in 'infinity' (i.e., Workfunction).

Modeling of the inhibition of corrosion

As the corrosion of Iron is driven by it donating the electrons, we expect our inhibitor to accept charge from the surface. For that purpose we calculate the prospective charge transfers: both from the molecule and surface separated (ΔN_{free}) and correlated ($\Delta N_{\mathrm{correl}}$). Additionally we perform the Bader charge analysis [4], to calculate the effective charge transfer ($\Delta N_{\mathrm{Bader}}$).

As shown both in the Table below and in the Figure on the right, there are three groups of compounds behaving differently in the calculations: *(i)* pure 1-aktyl-3-methyl-imidazoles; *(ii)* molecules supplemented by halogens; *(iii)* molecules supplemented by hydrogen sulphate.



	E_f	E_{HOMO}	E_{LUMO}	η	χ	$\Delta N_{\mathrm{correl}}$	ΔN_{free}	$\Delta N_{\mathrm{Bader}}$
BMIM	-2.20	-8.40	-4.30	2.05	6.35	0.76	0.68	0.76
HMIM	-2.18	-8.58	-4.46	2.06	6.52	0.84	0.70	0.68
OMIM	-2.18	-8.11	-4.29	1.91	6.20	0.74	0.70	0.66
BMIB	-2.41	-5.55	-1.86	1.84	3.71	-0.64	-0.21	**-0.36**
HMIB	-2.32	-6.48	-1.75	2.36	4.12	-0.31	-0.22	**-0.53**
OMIB	-2.29	-6.46	-1.76	2.35	4.11	-0.32	-0.22	**-0.81**
BMIC	-2.41	-5.70	-1.77	1.97	3.73	-0.59	-0.20	**-0.58**
HMIC	-2.40	-5.74	-1.77	1.98	3.75	-0.57	-0.22	**-0.62**
OMIC	-2.30	-6.66	-1.74	2.46	4.20	-0.27	-0.22	**-1.08**
BMIS	-2.43	-5.87	-1.85	2.01	3.86	**-0.52**	-0.31	-0.16
HMIS	-2.46	-5.60	-1.81	1.89	3.70	**-0.68**	-0.32	-0.13
OMIS	-2.49	-5.46	-1.72	1.87	3.59	**-0.79**	-0.32	-0.11

The Fermi energy, HOMO/LUMO energies, hardness, and electronegativity (all in eV), as well as three types of the calculated charge transfer.

(i) (marked in yellow) does not accept electron in either of the models. *(ii)* and *(iii)* exhibit weak inhibiting properties in the free-molecule model [5] but the Bader charge analysis shows *(ii)* to be strong acceptors, contrary to *(iii)*.

Nevertheless, the analysis of the prospective charge transfer of a correlated system indicates the inhibiting behavior is enhanced-but-not-reached most probably due to the system size.

Iron surface

To model iron surface we minimize the surface energy γ for different slabs, with the area A exposed to vacuum.

	energy (eV/♂)	A (Å^2)	γ (eV Å^{-2})	γ (J m^{-2})
bulk	-8.34069			
Fe(100)	-8.12508	74.132	0.157	2.52
Fe(111)	-7.92548	128.401	0.175	2.80
Fe(110)	-8.04459	69.893	0.153	2.44
W.R. Tyson and W.A. Miller [2]				2.41
I. H. Sahputra *et al.* [3]				2.44

Molecules in question

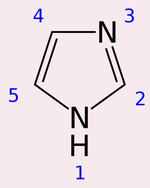
For simplicity we used a four-letter acronyms for 1-**ALKYL**-3-**m**ethylimidazolium **GROUP** molecule

alkyl	formula	symbol	group	formula	symbol
butyl	$-C_4H_9$	**B**	–	Ø	**M**
hexyl	$-C_6H_{13}$	**H**	Bromide	Br	**B**
octyl	$-C_8H_{17}$	**O**	Chloride	Cl	**C**
			Hydrogen sulphate	$-HSO_4$	**S**

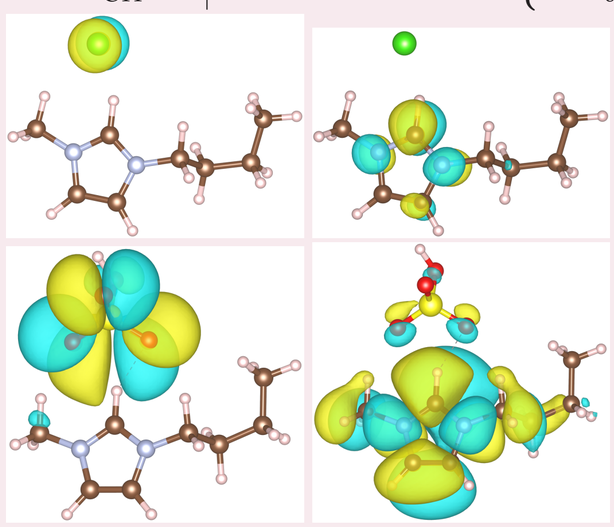
Hence, 1-octyl-methylimidazolium is being referred as **OMIM**, whereas 1-butyl-methylimidazolium bromide as **BMIB**.

Ionization

The effective charge on each atom of a 1-butyl-3-methyl-imidazolium. The numbering of carbon and nitrogen atoms corresponds to the schematic figure on the left.



	BMIM	BMIB	BMIC	BMIS
H(BrCl)		-0.8	-0.8	
C(1)	0.3	0.2	0.2	0.2
C(2)	0.7	1.0	1.0	1.1
C(3)	0.4	0.3	0.3	0.3
C(4)	0.4	0.4	0.4	0.3
C(5)	0.4	0.4	0.4	0.5
N(1,3)	-1.3	-1.4	-1.4	-1.4
S			−0.9	3.9
O				-1.4
OH				-0.6



Density plots of the HOMO (left) and LUMO (right) wavefunctions for 1-butyl-3-methyl-imidazolium chloride and 1-butyl-3-methyl-imidazolium hydrogen sulphate.

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See more at `www.md-esg.eu`.

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